

Thermodynamics of the Adsorption of Cd(II) from Aqueous Solution on NCRH

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Abstract— Batch kinetic studies were conducted for the adsorption of Cd(II) on NCRH. At the adsorbent dose of 10 g/l and initial Cd(II) concentration of 10 mg/l, 93 to 97 % removal were observed when the temperature increases from 15° to 40°. Equilibrium time was found to be 60 min. This paper attempts to develop simple and easily understandable thermodynamic parameters related sorption process at the equilibrium. The overall scenario represented by thermodynamic parameters was found to be a better indicator of understanding the process mechanism. Sorption of Cd(II) on NCRH followed pseudo second-order kinetic equation. The standard Gibbs free energy ΔG° value for the adsorption processes of Cd(II) was obtained as -7.30 kJ/mole. The negative value, ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. The values of ΔH° and ΔS° for Cd(II) were obtained as 26.4, kJ/mol and 113.2 J/mol respectively. The positive value of ΔH° indicates endothermic nature of adsorption, while positive ΔS° value confirms the increased randomness at the solid-liquid interface during adsorption. The activation energy for the sorption of Cd(II), was found as 11.37 kJ/mol indicating chemisorption.

Index Terms— Activation energy, Gibbs free energy, NCRH, Cadmium, Thermodynamics, Adsorption.

I. INTRODUCTION

Cadmium is a metal widely used in industries such as cadmium plating, alkaline batteries, copper alloys, paints and plastics. It is a non-essential and non-beneficial element to plants and animals. Its toxic effects are well documented. Diseases such as renal damage, anemia, hypertension and itai-itai are associated with excess cadmium [1], [2]. Hence it is important to eliminate trace of cadmium from drinking water, or to remove cadmium from wastewaters before they are discharged into receiving bodies. In our continued study on the use of low-cost material for the removal of organic and organic pollutants from water and wastewater we investigated rice husk as a sorbent for the removal of Cd(II). Some simple and low-cost chemical modifications resulted in increasing the sorption capacity of raw rice husk. The highly efficient low cost and the rapid uptake of Cd(II) by NCRH indicated that it could be an excellent alternative for the removal of heavy metal by sorption process [3]. This paper attempts to develop simple and easily understandable thermodynamic parameters related sorption process at the equilibrium, such as as entropy change, enthalpy change, Gibbs free energy and activation energy of sorption. The overall scenario represented by thermodynamic parameters

was found to be a better indicator of understanding the process mechanism

II. MATERIALS AND METHODS

A. Preparation of NCRH

Fresh rice husk was obtained from a local rice mill and was passed through different sieve size. The fraction of particle between 425 and 600 μ m (geometric mean size: 505 μ m) was selected [3]. Rice husk was washed thoroughly with distilled water and was dried at 60 °C. This was treated with 0.1 mol/l sodium carbonate solution at room temperature for 4 h. Excess of sodium carbonate was removed with water and the material was dried at 40 °C. Sodium carbonate treated rice husk was designated as NCRH [3].

B. Batch Kinetic Studies

All chemicals used were of analytical grade (E. Merck, India). Stock solutions of 1000 mg/l was prepared for Cd(II) using cadmium nitrate. In order to avoid hydrolysis as well as high adsorption of species in the flask wall the stock solution was prepared with HNO₃ 2% (v/v), which were diluted with distilled water to prepare working solutions. pH of the working solutions were adjusted to 6.8 \pm 0.2 for all studies using dilute NaOH solution. The experiments were carried out with 10 g/l of sorbent dose for initial metal concentration of 10 mg/l. The mixture was agitated using a thermostatic rotary shaker at 180 rpm in the temperature range of 15° – 40 °C. At the end of the experiment the sample was allowed to settle for about 1 min and the supernatant sample was analyzed for its Cd(II) concentration using atomic absorption spectrophotometer (AA-6650, Shimadzu, Japan).

III. RESULT AND DISCUSSION

A. Effect of Temperature

The removal kinetics of Cd(II) by NCRH were obtained at 15°, 25° and 40° C (Fig. 1). At an equilibrium time of 60 min for initial Cd(II) concentration of 10 mg/l, the percentage removal increases from 93 to 97 % with the increase in temperature from 15° to 40° C (Fig. 2).. The sorption capacity increases with increase in temperature indicating that the sorption process was endothermic and the sorption of metal ions by NCRH may involve not only physical but also chemical sorption [4]. The increase in sorption capacity of NCRH at high temperature may be attributed to enlargement of pore size or increase in the active surface for sorption. This could also be due to the enhanced mobility of the metal ions from the bulk solution

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towards the adsorbent surface and extent of penetration within NCRH structure overcoming the rate of intraparticle diffusion [4], [5].

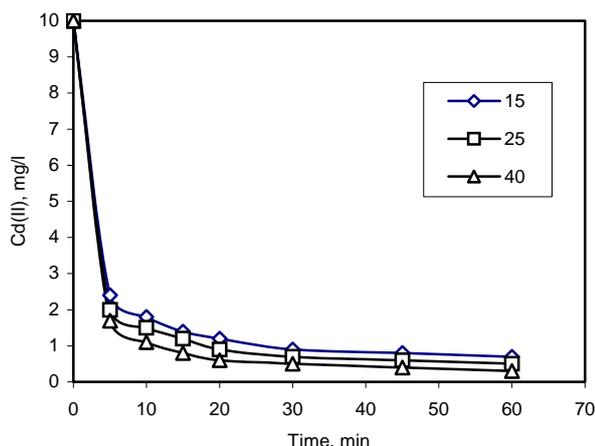


Fig. 1. Kinetic profile of Cd(II) uptake at 15, 25 and 40 °C.

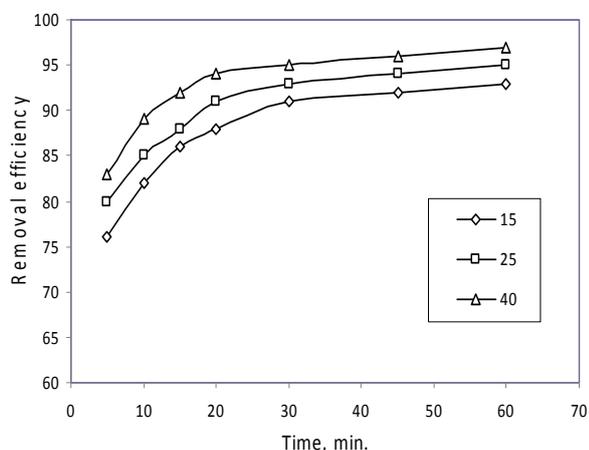


Fig. 2. The rate of removal efficiency of Cd(II) at 15, 25 and 40 °C.

B. Sorption Kinetic

Pseudo second-order kinetic model has been widely used for the sorption kinetics [6]-[8]. It was observed that most of the sorption systems followed a pseudo second-order kinetic model as also reported by Ho and McKay [6], which can be expressed as

$$\frac{t}{q} = \frac{1}{h_0} + \frac{t}{q_e} \quad (1)$$

The initial sorption rate can be obtained as t approaches zero ($t \rightarrow 0$):

$$h_0 = K_{p2} q_e^2$$

where h_0 is the initial sorption rate (mg/g min), t is the contact time (min), q and q_e are the quantities of sorbate (in mg/g), sorbed at time t and at equilibrium respectively and K_{p2} is the rate constant (g/mg min). The rate constant K_{p2} was found out from the slope of the linear test plot between t/q versus time t as shown in Fig. 3. The values of K_{p2} for 15°, 25° and 40° C was obtained as 0.697, 0.763 and 1.011 g/mg min respectively.

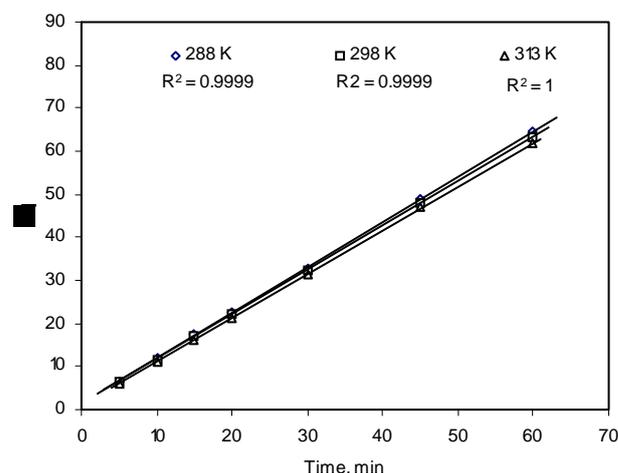
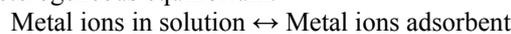


Fig. 3. Pseudo second order model plot for Cd(II) at different temperature in K.

C. Thermodynamic Parameters of Adsorption

The adsorption process of metal ions can be summarized by the following reversible process, which represents a heterogeneous equilibrium.



The apparent equilibrium constant (K_c) of the adsorption is defined as:

$$K_c = \frac{C_A}{C_e} \quad (2)$$

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where C_A is the solid phase concentration at equilibrium (mg/l), C_e is the equilibrium concentration (mg/l), T (K) the absolute temperature, R the gas constant (8.314 J/mol K), ΔS° the entropy change (J/mol) and ΔH° the enthalpy change (kJ/mol). ΔH° and ΔS° values were obtained from the slope and intercepts of van't Hoff plot, $\ln K_c$ versus $1/T$ (Fig. 4). The K_c value thus obtained is also used to determine the Gibbs free energy ΔG° at 25 °C. The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favorable adsorption [10]-[13]. The standard ΔG° values for

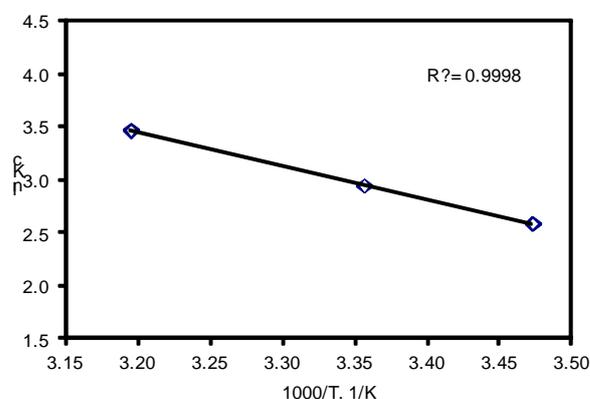


Fig. 4. van't Hoff plots for Cd(II)

the adsorption processes of Cd(II), was obtained as -7.30 , kJ/mole respectively using equation (3). The negative value ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption [10]-[13]. The values of ΔH° and ΔS° for Cd(II), was obtained as 26.4 , kJ/mol and 113.2 J/mol respectively. The positive value of ΔH° indicates endothermic nature of adsorption while positive ΔS° value confirms the increased randomness at the solid-liquid interface during adsorption [10]-[13].

D. Activation Energy

The increase in the pseudo-second order rate constant with temperature may be described by the Arrhenius equation which is used to calculate the activation energy for the metal ion sorption [4], [5], [9] as given below:

$$\ln k_{p2} = \ln A_0 - \frac{E_a}{RT} \quad (5)$$

where k_{p2} is the rate constant of sorption (g/mg min), A_0 is the temperature-independent factor (g/mg min), E_a the activation energy of sorption (kJ/mol), R the gas constant (8.314 J/mol K) and T the solution temperature (K). The kinetic profile of Cd(II) uptake at 15 , 25 and 40° C as shown earlier in the Fig. 1 was utilized to find the rate constant k_{p2} from the pseudo second order plot (Figs. 2)

When $\ln k_{p2}$ is plotted versus $1/T$, a straight line with slope $-E_a/R$ is obtained. The magnitude of the activation energy may give an idea about the type of sorption. Two main types of adsorptions may occur: physical and chemical. In physical adsorption equilibrium is usually rapidly attained and easily reversible, because the energy requirement is small (usually no more than 4.2 kJ/mol) and since the forces involved are weak. Chemical adsorption is specific and involves forces much stronger than physical adsorption. So the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions which means that the rate varies with temperature according to finite activation energy (between 8.4 and 83.7 kJ/mol) in the Arrhenius equation [4]. The activation energy for the sorption of Cd(II), was found as 11.37 , kJ/mol respectively from the slope of Fig. 5 indicating chemisorption.

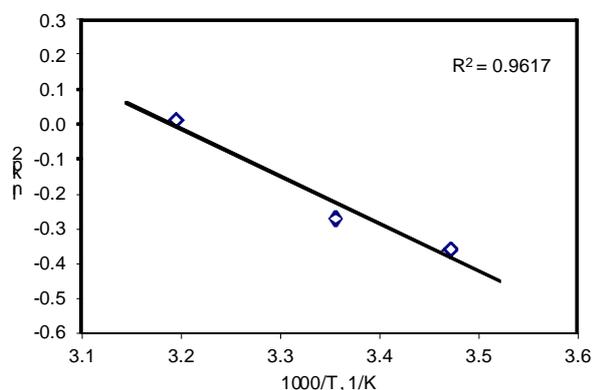


Fig. 5. $\ln k_{p2}$ vs. $1/T$ plots for Cd(II)

IV. CONCLUSION

Batch kinetics studies showed a rapid removal of Cd(II) by NCRH and it increases with increase in temperature. The sorption systems followed a pseudo second-order kinetic model with very high correlation coefficients. The sorption

process was endothermic and it was further conformed by the positive value of ΔH° (26.4 kJ/mol) and further positive value of ΔS° (113.2 J/mol) confirms the increased randomness at the solid-liquid interface during adsorption. The standard Gibbs free energy ΔG° value for the adsorption processes of Cd(II) was obtained as -7.30 kJ/mole. The negative value, ΔG° confirms the feasibility of the adsorption process and spontaneous nature of adsorption. The activation energy for the sorption of Cd(II), was found as 11.37 kJ/mol indicating chemisorption.

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